Batch tests to examine the role of Inorganic Carbon in the recovery of phosphate as calcium phosphate

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Wastewater from potato processing industry is of valuable interest for **phosphate recovery**. Struvite ($MgNH_4PO_4.6H_2O$) precipitation is applied successfully on some anaerobic treated wastewaters, but it has a rather low commercial value. **Calcium phosphate** may be a more appropriate alternative for re-use applications, at least if it is harvested in a pure, qualitative product. The following batch experiments, performed on anaerobic wastewater from a potato processing plant, show that the removal of both ammonium and total inorganic carbonate (TIC) strongly contributes to this requirement.

Experiment 1: Influence of pH and $[Ca^{2+}]/[P]$ ratio

The collected wastewater was characterized as follows: pH 7.3; NH_4^+-N 145 mg/L; K^+ 754 mg/L; Ca^{2+} 58 mg/L; Mg^{2+} 55 mg/L; PO_4^{3-}-P 83 mg/L and TIC 396 mg/L.

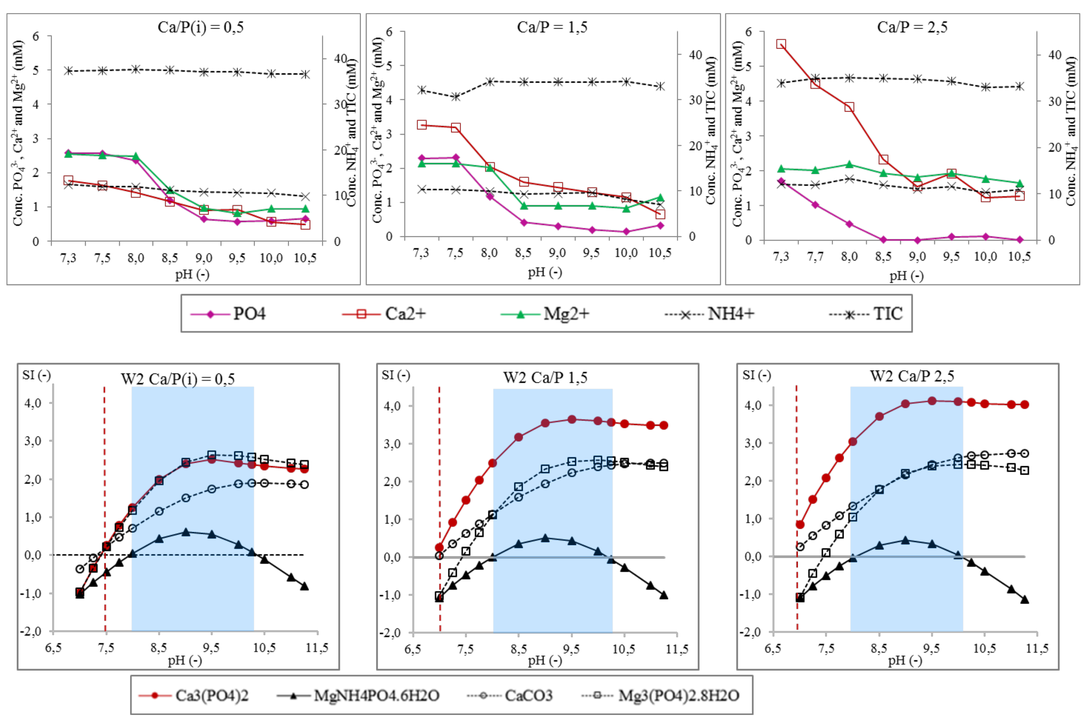

Figure 1 Residual ion concentrations after 1 hour of reaction time when increasing the pH with NaOH 1M; the experiment was carried out on the original wastewater ($[Ca^{2+}]/[P]$ ratio = 0.52) and after increasing the $[Ca^{2+}]/[P]$ ratio to 1.5 and 2.5. The experiment was supported with the calculation of some SI-values.

- The **Saturation Indexes** (SI) of struvite, calcium and magnesium phosphate and calcium carbonate are calculated with the PHREEQC program (Parkhurst *et al.*, 1999). A positive SI means oversaturation.
- Despite its positive SI between pH 7.5 and 8.5 in the wastewater, calcium phosphate does not precipitate.
- Increasing pH with NaOH above pH 8.5 leads to precipitation of **struvite**.
- Adding Ca^{2+} in order to increase the $[Ca^{2+}]/[P]$ ratio to 2.5 yields full recovery of phosphate as **calcium phosphate** at pH 8.5.
- In some cases, a further increase of pH results in the simultaneous precipitation of **calcium carbonate**, this is derived from the almost equimolar removal of calcium and TIC.

Experiment 2&3: Influence of (bi)carbonate and ammonium

- Removing all TIC improved recovery of phosphate. In the absence of TIC and starting from pH 8.5, magnesium phosphate precipitated. In the presence of TIC also calcium carbonate seems to precipitate. Increasing the pH with Na_2CO_3 1M invariably led to low phosphate recoveries. The quick formation of soluble complexes as $Ca_2HPO_4CO_3$ and $Ca_2PO_4CO_3^-$ is presumed (Pan and Darvell, 2010).
- No struvite is precipitating within the absence of ammonium. At pH 8.5, the precipitate appears to be pure calcium phosphate with a good yield of phosphate removal (75%) at a $[Ca^{2+}]/]P]$ ratio of 1.5. Magnesium phosphate precipitation started from pH 10.

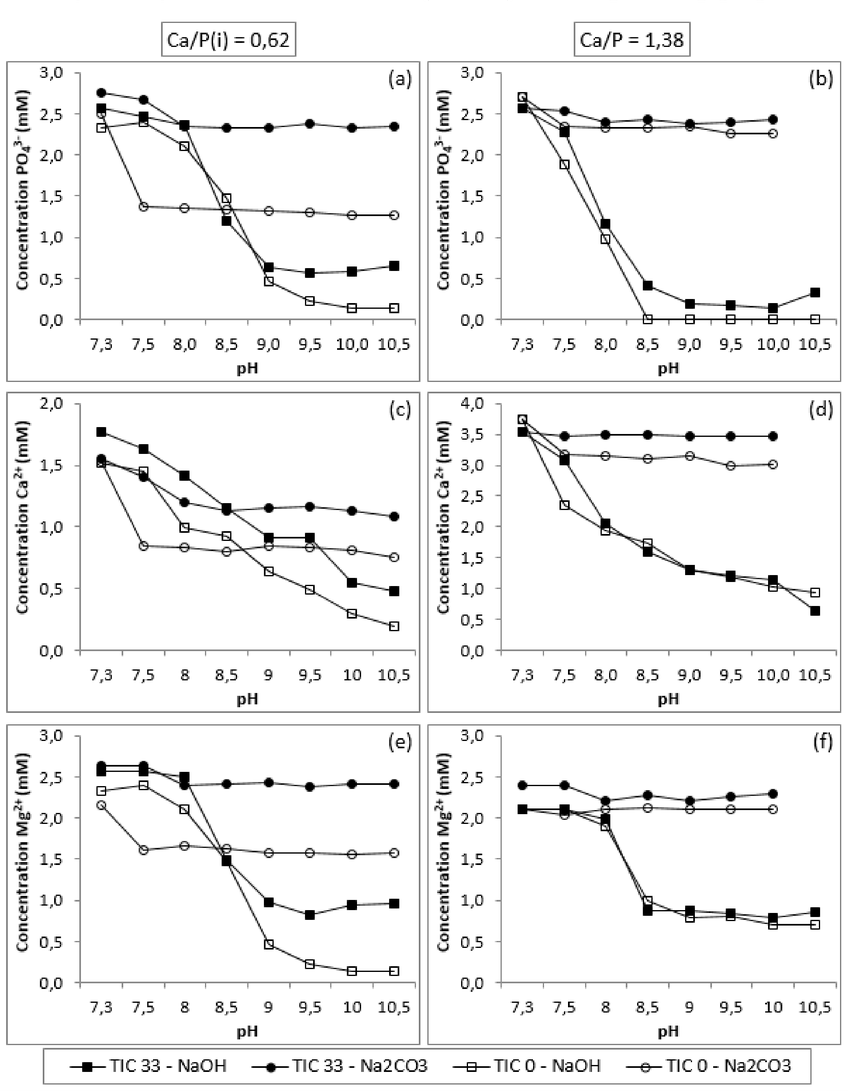

Figure 2 Residual ion concentrations after 1 hour of reaction time when increasing the pH with NaOH 1M or Na_2CO_3 1M of the original the wastewater (see experiment 1, TIC = 33 mM) and after removing TIC (TIC = 0) by aeration under a constant pH; the experiment was carried out without ($[Ca^{2+}]/[P]$ ratio = 0.62) and with prior addition of extra Ca^{2+} ions ($[Ca^{2+}]/[P]$ ratio = 1.38).

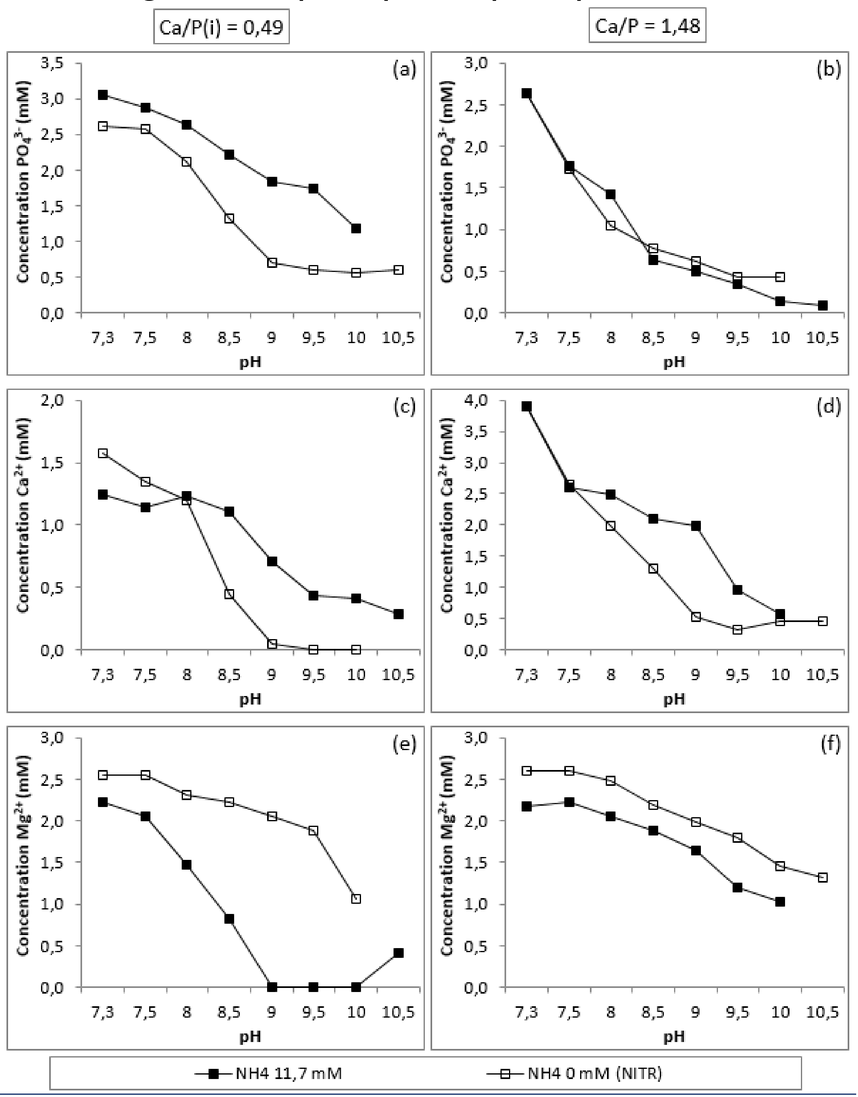

Figure 3 Residual ion concentrations after 1 hour of reaction time when increasing the pH with NaOH 1M of the wastewater after nitrification (NH4 0 mM, TIC 9,6 mM) and of the wastewater with a reduced TIC concentration by aeration (NH4 11,7 mM, 9,6 mM TIC); the experiment was carried out without ($[Ca^{2+}]/[P]$ ratio = 0.49) and with prior addition of extra Ca^{2+} ions ($[Ca^{2+}]/[P]$ ratio = 1.48).

Conclusion

The removal of the buffering compounds **ammonium and bicarbonate** seems to pave the way to phosphate removal as calcium phosphate at rather low pH levels. In practice, the removal of both can be achieved with the biological **nitrification** process. In that case, the TIC/TAN (Total Ammonium Nitrogen) ratio is of importance:

$$NH_4^+ + 1{,}5\ O_2 \rightarrow NO_2^- + H_2O + 2\ H^+$$
$$NO_2^- + 0{,}5\ O_2 \rightarrow NO_3^-$$
$$+\quad 2\ H^+ + 2\ HCO_3^- \rightarrow 2\ H_2CO_3 \rightarrow 2\ CO_2\uparrow + 2\ H_2O$$
$$\mathbf{NH_4^+} + 2\ O_2 + \mathbf{2\ HCO_3^-} \rightarrow NO_3^- + 2\ CO_2\uparrow + 3\ H_2O$$

It is concluded that the nitrification of anaerobic treated wastewater will result in the precipitation of calcium phosphate with no/lesser struvite and carbonate interferences. Furthermore, smaller volumes of alkali are necessary to achieve the required pH increase in comparison with the currently applied struvite process.